UDC 666.1.053.562.002.2(047)

THE EFFECT OF ADDITIVES AND IMPURITIES IN TIN ON ITS OXIDATION AND INCORPORATION INTO THE BOTTOM SURFACE OF FLOAT GLASS (A REVIEW)

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Translated from Steklo i Keramika, No. 3, pp. 6 – 9, March, 2001.

Based on the patent information, scientific literature, and research done by the Saratov Institute of Glass, the effect of additives and impurities in tin on the quality of float glass is determined. The mechanism of an effective metallic additive is clarified. An activity progression of impurity components in tin with respect to oxygen and sulfur is arranged, and on its basis it is possible to estimate and predict the effect of the additives on the reactions between tin and glass and control the glass quality.

One of the main conditions for ensuring a high-quality surface in float glass is the absence of contaminating impurities in the gas space of the melting tank and in the tin melt.

When these conditions are satisfied, the interaction between tin and glass remains weak. However, the situation changes significantly when even a slight quantity of oxygen and sulfur emerges in the protective gas atmosphere, or when small amounts of certain metallic impurities are present in the tin melt [1 – 4].

Oxygen and sulfur react with the tin forming SnO and SnS, which partly incorporate into the tank atmosphere, get condensed on the tank roof, and then precipitate in the form of drops on the upper surface of the glass, impairing its quality.

It should be noted that under a shortage of oxygen, SnO is formed, and with an excess of oxygen, the resulting compound is SnO_2. The bivalent tin ion Sn^{2+} (even when bonded to oxygen) has an elevated diffusion capacity, compared to metallic tin atoms or the tetravalent tin ion Sn^{4+}. Being a modifier of the vitreous state, the Sn^{2+} ion is easily incorporated in the glass structure. It can be assumed that reactions between tin and glass are the most intense under the conditions that facilitate the formation of SnO.

Thus, SnO can diffuse into the bottom surface of glass, modifying the glass composition and properties. In particular, under secondary heating, glass with an increased content of tin in the bottom layer acquires the typical texture with iridescent luster, which is classified as a defect and prevents the application of this glass.

In contrast to the above, the opportunities of SnO_2 for reacting with glass are significantly more limited: the diffusion of Sn^{4+} ion in the glass melt is impeded due to the high charge of the ion. Therefore, SnO_2 can penetrate into the glass structure mainly through the dissolution of SnO_2 or emerging stannates in the glass melt, or as the consequence of oxidation of Sn^0 and Sn^{2+} which have diffused into the glass melt. Therefore, SnO_2 is mostly manifested as slag on the melted tin surface, which is entrained from the melting tank by the bottom surface of the glass band and contaminates the transporting rolls of the annealing furnace. All this impairs the quality of the glass surface.

Certain impurities in tin transform into slag as well and, similarly to SnO_2, impair the surface quality or actively react with the glass and form polycrystalline films on the glass surface.

In spite of the fact that the content of oxygen and sulfur in the protective atmosphere is significantly restricted, these elements are inevitably present in the melting tank, since the glass contains the specified elements. They can also penetrate into the melting tank from the outside air and the atmosphere of the glass-melting furnace.

That is why a protective atmosphere is constantly supplied to the melting tank. It contains up to 90% nitrogen and up to 10% hydrogen, which ensures the redox reaction processes:

$$Sn + \frac{1}{2} O_2 \rightarrow SnO;$$

$$SnO + \frac{1}{2} O_2 \rightarrow SnO_2;$$

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$$Sn + O_2 \rightarrow SnO_2;$$

$$2SnO \rightarrow 2SnO_2 + Sn;$$

$$Sn + H_2O = SnO + H_2;$$

$$SnO + H_2O = SnO_2 + H_2;$$

$$Sn + 2H_2O = SnO_2 + 2H_2.$$

Some analogous reactions take place as well when sulfuric compounds act as oxidizing components.

Depending on the temperature, the partial pressures of the gaseous components, and other factors, both oxide formation and oxide reduction reactions can occur in the process conditions. In particular, the last three reactions can be directed to the formation of tin oxides in such zones of the melting tank in which the penetration of hydrogen for some reasons is impeded, for instance, in places of contact between the melted tin and the glass. Furthermore, substantial penetration of air is possible in the site where the glass band exits from the tank. In this case, the presence of only one gaseous reducing agent, namely, hydrogen, can be insufficient.

Hydrogen is capable of dissolving in small quantities in the tin melt and thus facilitates the reduction of tin oxides in the surface layer of glass bordering on the metal melt. However, the quantity of this reducing agent in the contact zone is limited by poor solubility of hydrogen.

The patent literature (Gr. Britain Patents Nos. 1014514 and 1014515; France Patents Nos. 1364538 and 1364539) proposed introducing special additives of various elements to the tin melt, which are capable of reducing tin oxides or preventing tin oxide formation, due to the more intense reactions with oxygen, water steam, carbon dioxide, and sulfuric compounds. Numerous elements are suggested as such additives: lithium, sodium, potassium, magnesium, calcium, barium, zinc, aluminum, indium, carbon, silicon, titanium, zirconium, vanadium, niobium, chromium, manganese, and iron.

The great variety of the recommended elements complicates the selection of the most efficient additives. The patents indicate that the effect of the additives is based on the deoxidization (reduction) of tin oxides or on preferential reactions with oxygen and sulfuric compounds. With respect to lithium, sodium, potassium, magnesium, calcium, zinc, barium, indium, and iron, the patents briefly indicate that these elements or, rather, their oxides in the formation of a polished glass band can dissolve in the surface layer of glass without impairing its qualities; therefore, they are preferable.

The oxides and other compounds of such elements can incorporate in the glass structure only in limited quantities. Their excessive portions, as well as the products of oxidation of all other metallic additives, persist in the reaction zones and keep floating over the melted tin surface. In relation to this, the patents state that it is necessary to remove them from the melt tank by a mechanical or some other method. No further recommendations are supplied regarding the mechanism of the action of metallic additives, their behavior in the technological process, and the reactions of these additives or their oxides with glass, sulfuric compounds, and the gas atmosphere components. Any considerations of the economical aspects of the application of additives are absent, and neither are there data on whether the specified additives are used in practice.

The Saratov Institute of Glass carried out research on the effect of sodium, aluminum, calcium, and magnesium additives, as well as their combinations, on the quality of glass.

It was determined that the mechanism of action of an efficient metallic additive can be reduced to the following main reactions:

– reaction of the metallic additive with the oxidizing gas components in the zone of contact between glass and tin:

$$2Me + O_2 = 2MeO;$$

$$Me + H_2O = MeO + H_2;$$

– reduction of tin oxides in the same zone:

$$2Me + SnO_2 = 2MeO + Sn;$$

$$Me + SnO = MeO + Sn;$$

– reaction of the metallic additive oxide with glass and its complete or partial incorporation into the glass structure without impairing the glass surface properties;

– regeneration of the metal additive through the reduction of its oxides by hydrogen in the zone of contact of the tin and the protective atmosphere (as one of the variants):

$$MeO + H_2 \rightarrow Me + H_2O.$$

Moreover, the efficiency of the introduced additive significantly depends on its concentration. It is established that aluminum has a positive affect only when introduced in small quantities. With a substantial concentration, the aluminum oxidation products form solid phase particles, which leads to the formation of microbubbles impairing the glass surface. The products of reactions between sodium and magnesium and the gases released from the glass are significantly more soluble in glass. However, it is not advisable to introduce large quantities of sodium either, since this leads to a significant decrease in the surface tension, which increases the bubble growth rate. The Saratov Institute of Glass has developed a unit for introducing additives into tin melt (USSR Inventor's Certif. No. 333138).

A study of the IR spectra and microphotos of a series of glasses demonstrated that the introduction of certain inhibitors results in a significant decrease in the number of microbubbles and the disappearance of a dull film on the glass surface.

It was established that the amount of tin incorporated into the glass becomes significantly lower on adding the inhibitors. According to the chemical analysis data, the tin content in the glass surface layer after the introduction of magnesium decreased by half. This can be accounted for by the

decreased amount of bivalent tin in the melt, due to the reduction of the latter by the inhibitors. The bivalent tin reacts most intensely with the glass. The atomic or tetravalent tin at the process temperature does not become incorporated in the glass structure in significant quantities.

Finally, the specified additives have another significant advantage: they are relatively inexpensive and easily available.

Thus, the introduction of inhibitors into tin melt prevents the formation of tin oxides and decreases the amount of tin incorporated in the glass.

It should be noted that the existent Russian standards impose a number of limitations for copper, zinc, iron, and other metal impurities in tin (GOST 860–75). However, the motivation for these restrictions, except for temperature limitations, is not clear.

It is believed that the metals whose oxygen activity exceeds the oxygen activity of tin constitute toxic impurities in tin. Therefore, it is necessary to rank in the oxygen activity progression the impurity components in tin. For this purpose, the variations in Gibbs thermodynamic potentials ΔZ_T^0 [5, 6] of oxide formation were calculated for these metals. The higher the absolute values of ΔZ_T^0, the higher the metal activity. Based on this characteristic, all the metals can be arranged in the following progression: Cu → Bi → Pb → As → Ni → Sb → Co → Cd → Sn → Fe → Zn → Na → Al → Mg → Ca.

The metals in this progression that are ranked to the right of tin are capable of being oxidized by oxygen dissolved in tin, and accordingly, their presence in tin is undesirable. The impurities of copper and zinc in tin are not toxic, since these metals are ranked to the left of tin in the activity progression.

It is possible to arrange a similar progression for the activity of the metals with respect to sulfur: As → Sb → Bi → Sn → Ni → Co → Fe → Cu → Cd → Pb → Zn → Al → Mg → Na → Ca.

Judging from the data of this progression, copper and zinc in tin are undesirable elements, as their activity with respect to sulfur is higher than that of tin. However, an increase in the content of each of these elements in tin up to 0.1 and more wt.% on the ÉPKS-4000 production line did not lead to the formation of bubbles. This suggests that even if the reaction of the specified metals with sulfur in tin may result in the formation of sulfide compounds, this can only occur at higher concentrations of the metals, as well as of sulfur.

Certain data indicate that copper additives in combination with tin produce alloys with high bond energy and decrease the tin activity in the melt. Lead, on the other hand, activates tin and contributes to its oxidation.

It is established that the evaporation of sulfides from the melting tank can be reduced by using a melted alloy of tin with about 30% copper and removing the sulfides from the chamber by chilling parts of the alloy, in order to convert the sulfides into the insoluble form (U.S. Patent No. 4406682).

This is due to the fact that sulfur preferentially reacts with copper, in accordance with the sulfur activity progression of metals. As the evaporativity of copper sulfide is lower than the evaporativity of tin, the melted metal can accumulate larger amounts of sulfur, which has a lower volatilization, than in using exclusively tin. Furthermore, sulfides from the tin – copper alloy are transformed into the insoluble form at higher temperatures than sulfides from the pure tin melt. The insoluble sulfides float on the melted alloy surface and can be removed from the float tank.

Thus, the following conclusions can be made:

– the presence of copper impurities in tin (within reasonable limits) does not affect the technological parameters of the glass molding process;

– the question of the toxic effect of lead impurities in tin remains open, since the available data are contradictory.

Let us now consider the effect of iron impurity in tin on float glass formation.

On the one hand, there are published data on the favorable effect of ferric impurities in tin. Thus, the Department of Physical Chemistry of Inorganic Materials of IMP of the Academy of Sciences of Ukrainian SSR carried out systematic integrated research to clarify the physicochemical phenomena of the reactions between glass melt and melted metals. With this aim, a unit for heat-treatment of glass melt bars in contact with tin-based melts was developed [7].

The glass melt used in this research had the following composition (%): 74.6 SiO_2, 8.7 CaO, 15.7 Na_2O, 0.65 SO_3, and the rest was Al_2O_3, Fe_2O_3, MgO, and Sb_2O_3. The glass melt was extracted from the working channel of a continuous glass-melting furnace and cast in the form of briquets, which were subsequently split into separate samples. The metallic melt was tin of "extra pure" grade, or alloys based on this tin which were previously melted from pure components in a protective gas medium.

The neutron activation analysis of the solutions of layers obtained in studying the samples established that in the melt containing 99% Sn and 1% Fe, the iron virtually does not diffuse into the glass.

Apparently, in this particular case, the iron impurity on the interface between the metallic melt and the glass melt reduces the oxidizing agents (including sodium ions that are part of the glass melt) to such an extent that the formation of tin ions on the interface boundary in the temperature interval 800 – 1100°C becomes thermodynamically disadvantageous, and thus the mass transfer of tin into the glass melt is blocked.

On the other hand, the data obtained on the experimental production line indicate that iron in tin is an undesirable impurity. For various reasons, 2 – 3 months after putting in operation the ÉPKS-4000 production line, the iron content in the tin grew from 0.01 to 0.06 % and more. This led to the formation of small open bubbles, which were eliminated after the tin was purified from iron. The purification was carried out by remelting the tin at temperatures of 300 – 350°C during the reconstruction of the melting tank. Since the solubi-

lity of iron in tin abruptly decreases with a decreasing temperature, low-temperature remelting caused the formation of a condensed phase of ferric compounds in the tin. As a result, it became possible to reduce the iron content to 0.01% or less. The experimentally found maximum admissible concentration of iron impurity in tin was 0.04 – 0.05%. The optimum iron content is 0.01 – 0.03%.

In other words, there is a discrepancy between the experimental data and the results obtained in [7]; therefore, it is necessary to continue studying the effect of iron impurities in tin on the process of float glass formation, employing contemporary methods.

Thus, according to the data of the technical literature and the studies carried out by the Saratov Institute of Glass, it is possible to efficiently control the process of tin incorporation into the bottom surface of glass and the tin oxidation process by means of introducing additives (impurities) into the tin melt. Based on the oxygen and sulfur activity progressions of impurity components in tin, it is possible to estimate and predict their effect on the physicochemical processes in the reactions between tin and glass and to control the glass quality.

The results of the research performed by the Institute made it possible to solve the problem of stabilizing the float process and controlling the quality of the glass surface, and provided for deliberate control of the physicochemical process in float technology, with the purpose of modifying the glass surface and obtaining the prescribed properties.

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